A look at design and application of fuel cell systems

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Over the past few years, the direct conversion of chemical into electrical energy via fuel cells has been at the center of attention of electrochemical research and technology development. This is due not only to the complexity of fuel cell reactions and the general awareness of the technological potential of fuel cells but is also a result of society's strive towards developing environmentally-friendly power generation. In the reaction between hydrogen and oxygen for example, the only chemical product is water. The fuel cell, initially developed in the sixties as an on-board power supply unit for spacecraft, has now found new applications in powering submarines, in decentralized power supply systems, in portable charging docks for small electronics and in sensor technology. In the quest for a highly efficient, emission-free drive system, the development of mobile automotive fuel cell units is proving to be quite promising. Fuel cell technology constitutes a highly varied field which extends from available fuels and their processing, through the fundamentals of electrochemical processes, especially electro-catalysis, right to the numerous new concepts in systems technology for complete fuel cell aggregates including the control of gas, water and heat management. Many publications now appear annually in this field. The number of patent applications, especially from the industrial sector, has also risen over the past ten years. However, this paper is related to the design and application of fuel cell systems.

Key words: Design, fuel, cell systems, power generation.

INTRODUCTION

Continued reliance on current fuels and end-use technologies poses serious environmental and energy supply security challenges. Globally, direct combustion of fuels for transportation and heating accounts for over half of the greenhouse gas emissions, a large amount of air pollutant emissions and about two thirds of primary fossil energy use. Even with continuing incremental progress in reducing emissions and improving energy efficiency, most models of the future energy system project that energy use and emissions of greenhouse gases and air pollutants from fuels will grow over the next century, because of growing demand, especially in developing countries.

Electro-chemistry is concerned with the study of chemical reactions in a solution at the interface between an electronic and ionic conductor and has concentrated on:

I. The nature of the ionic conductors,
II. The structure of the electrified interface that forms an immersion of an electronic conductor into an ionic conductor, and
III. The electron-transfer processes that can take place between electrolyte/electrode and its limitations.

Electrochemical galvanic cells

Galvanic cells are electrochemical cells in which the electrode reactions take place spontaneously which leads to electrical current and are capable of the direct conversion of chemical to electrical energy. The most important types of galvanic cells are batteries and fuel cells. The main difference between them is that a battery carries its fuel around with it, whereas fuel must be
supplied from an external source to a fuel cell. Unlike a battery, a fuel cell cannot go flat. The fuel cells use hydrogen as the fuel and oxygen or air as the combustant.

Types of fuel cells

Fuel cells and electro-catalysts

The galvanic cell of the compound of an electrochemical cell operation with hydrogen and oxygen as fuel and combustant represents the archetypal fuel cell and the operation of such fuel cells, represents one of the most attractive goals of modern day electrochemistry. One immediate problem is that the fuel used is hydrogen, which is one of the major problems for fuel cells. All attempts to drive fuel cells directory using primary fuels such as coal oil, natural gas, etc. have failed at least with low-temperature devices; either high temperature or fuel reforming or both have proved necessary leading to high costs associated with the use of expensive catalysts or complex engineering. These inter-connected problems have bedeviled efforts to build commercially attractive fuel cell system. Since the work of Grove, more than 150 years ago, which led to the realization of the first simple fuel cell, hydrogen / oxygen fuel cells of steadily increasing efficiencies have been fabricated but this enhanced performance has not been sufficient, to justify the costs of isolation of H\textsubscript{2} from the primary fuels available.

The end of the 19\textsuperscript{th} century saw, initially in America, the rise of oil as a primary fuel and this led to renewed efforts to realize fuel cells based on direct hydro carbon oxidation at the anode. The emergence of natural gas as a major energy component has affected the equation in a number of ways; methane can perform with high efficiency. The purity of natural gas has also led to considerable advantages in terms of poisoning, allowing internal reforming as a possibility.

The alkaline fuel cell (AFC)

The alkaline fuel cell, using H\textsubscript{2} as a fuel, is the simplest low-temperature fuel cell in concept and operation. It operates at temperature of Ca 70°C and even at room temperature, has power level of Ca. 50% of those at the nominal operating temperature (Mclean et al., 2002).

The electrode construction is critically important in this, as in all low-temperature systems, with the primary requirements being:

a. Good electronic conductivity to reduce ohmic losses,
b. Adequate mechanical stability,
c. Chemical stability in the rather aggressive alkaline electrolyte, and
d. Stable electro-activity of the catalyst with time.

Normally, the electrodes are fabricated from a mixture of carbon and polytetra fluoroethylene (PTFE), the latter controlling both the macro-porosity of the electrode and its hydrophobicity. The primary cost of these electrodes lies in the catalysts most particularly for the cathode. The primary problems associated with the alkaline fuel cell are:

a. Operation in air is a problem due to the presence of CO\textsubscript{2}, which is absorbed into the alkaline electrolyte, generating the relatively insoluble K\textsubscript{2}CO\textsubscript{3} which in turn can deposit on and foul the cathode. CO\textsubscript{2} must therefore, be scrubbed from the air if it is used as the oxidant.
b. The poisoning of the electrodes, which is particularly severe for platinum, since the anode can be poisoned by traces of CO in the hydrogen, or by sulfur-containing compounds derived from the primary fuel.
c. Removal of the main combustion product, water, which would otherwise dilute the KOH and reduce performance.

The phosphoric acid fuel cells (PAFC)

The difficulties associated with the use of air as an oxidant in alkaline fuel cells sparked considerable interest in the exploration of acid media, where CO\textsubscript{2} would present fewer problems. The common mineral acids, however, present quite serious problems in this regard; adequate conductivities can only be attained at temperatures close to boiling.

Phosphoric acid at room temperature is only slightly dissociated, showing very low conductivity even in concentrated solution (Archer and Wimer, ????). However, at temperatures above Ca 15°C, the pure acid is found mostly in the polymeric state, as pyrophosphoric acid, which is a strong acid of high conductivity and the large size and low charge density of the polymeric anions leads to low chemisorptions on platinum, facilitating the oxygen reduction reaction. Other advantages of phosphoric acid include: good fluidity at high temperatures, tolerance to CO\textsubscript{2} and to moderate CO concentrations at higher temperatures, low vapor pressure, high oxygen solubility, low corrosion rate and large contact angle. The result is that, since its introduction in 1967, the phosphoric acid fuel cell has undoubtedly come to dominate the low temperature fuel cell market and is the only commercially available fuel cell. The basic principles of the cell are shown in Figure 1.

The development of the phosphoric acid fuel cell (PAFC) has taken two directions. The most important is the construction of relatively large stationary power units, such as 11 MW system at Goi, near Tokyo in Japan, with smaller systems in the US and Europe, which have allowed technologists to study in the operation of these
systems under real conditions.

**Molten carbonate fuel cell (MCFC)**

The basic principle of operation of molten carbonate fuel cells (Figure 2) (U.S. Department of Energy website; Marcenaro and Federici, 2005; Ghezel-Ayagh et al., 2005; Tooi, 2005) is that the cathode, made from porous lithiated NiO, the reaction is $\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO$, the electrolyte is an ionic mixture of 68% Li$_2$CO$_3$/K$_2$CO$_3$ at a temperature of 650°C. At the anode, made from a porous Ni/10 wt% Cr alloy. The reaction is $H_2 + CO_3 \rightarrow H_2O + CO_2 + 2e^-$. In a practical cell, the CO$_2$ produced at the anode must be transferred to the cathode, which can be carried out either by burning the spent anode steam with excess air and mixing the result with the cathode inlet stream, after removal of water vapor, or by directly separating CO$_2$ at the anode exhaust point. A major advantage of this cell is that CO, far from being a problem, can actually serve as the fuel, probably through the water-gas shift reaction.
Solid-oxide fuel cells (SOFC)

The principle operation of these cells is shown in Figure 3. Solid Oxide Fuel Cells are well known and increasing development has been undertaken since the 1960’s (Bossel, 1998). The characteristic features are an oxygen-ion conducting, solid electrolyte and the operating temperatures between 650 and 1000°C. At these temperatures, the electrode reactions are usually strong which allows for the use of notable electro-catalysts as electrodes. Both the electrodes and the electrolyte, form an all-solid-state-system while the reacting species (fuel and oxygen) are in the gas phase.

Only two phases (the solid and the gas phase) have to be handled in the solid oxide fuel cell (SOFC). This allows for various designs and concepts, since oxygen ions supplied by the electrolyte oxidize the fuel, both hydrogen and also carbon containing species such as CO, CH₄ or higher hydrocarbons can be utilized directly. These fuels are provided from fossil energy services, which are the main energy carriers to date.

During operation, both electrical power and heat are produced in the SOFC. The high operating temperatures lead to high quality heat, which makes the SOFC particularly suited for combined heat power production and combined cyde plants. However, the high operating temperatures also pose specific problems to the SOFC; materials must be compatible and physical properties such as the thermal expansion and dimensional stability in reducing and oxidizing environments are crucial. Therefore, high requirements are in materials. Particular problems are also imposed on the fuel cell periphery components, especially the high temperature stability and heat exchangers to control heat management of the SOFC. Up to 1995, cells operating at temperatures between 900 and 1000°C were developed for stationary applications in power plants. Since then, significant progress has been made in lowering the operating...
phenomenon is called non-faradaic electrochemical by the change in potential of the catalyst. This transfer through the interface. These electric forces are characterized by the so-called electrode potential which takes place as a heterogeneous reaction at the gas/metal interface as well as an electrocatalytic reaction at the electrolyte/electrode interface.

What is electro-catalysis?

Electrochemical reactions are connected with a transfer of electric charge through the interface electrode/electrolyte. The charge carriers can be ions or electrons. In the case of ions, the surface is continuously changing. Either by the deposition of ions or by the dissolution of electrode material (Kordesch, 1980). Additives to the electrolyte which are not consumed can increase the rate of ion transfer. For instance, small amounts of organic or inorganic species can accelerate the anodic dissolution of metals. In the case of electrons as charge carriers, the catalyst provides one of the reactants for the process, the electrons, which are either consumed or generated in the net reaction. The electrode surface remains unaffected after the reaction has reached a steady state.

In chemistry, homogeneous catalysis is a sequence of reactions that involve a catalyst in the same phase as the reactants. Most commonly, a homogeneous catalyst is co-dissolved in a solvent with the reactants. Homogeneous catalysts function in the same phase as the reactants but the mechanistic principles invoked in heterogeneous catalysis are generally applicable. Typically homogeneous catalysts are dissolved in a solvent with the substrates.

In contrast to heterogeneous catalysis, the driving force of an electrode reaction is not only controlled by parameters like concentration, pressure and temperature but also by electrical forces which affect the charge transfer through the interface. These electric forces are characterized by the so-called electrode potential which can be altered in an electrochemical cell by an external voltage. A change in potential leads to a change in electronic structure, e.g., to a change in electronic work function. Recent studies have shown that, the rate of a heterogeneous chemical reaction can also be influenced by the change in potential of the catalyst. This phenomenon is called non-faradaic electrochemical modification of chemical activity (NEMCA).

The closest connection between electrocatalysis and catalysis of a heterogeneous chemical reaction exists in the role of adsorption and chemisorptions of reactants or intermediates on the rate of the process. As an example, molecular hydrogen adsorbed at a metal surface, can be split into reactive hydrogen atoms. The necessary energy for breaking the bond is given as the heat of adsorption. This first step in the catalysis of the hydrogen reaction, takes place as a heterogeneous reaction at the gas/metal interface as well as an electrocatalytic reaction at the electrolyte/electrode interface.

The role of adsorption

Physisorption and chemisorption

Adsorption is a phenomenon of attraction of atoms and molecules that occurs at interfaces and leads to a concentration of the absorbed species in the interfacial region larger than the coverage concentration in the bulk fluid (gas or fluid) phase. There is a broad spectrum of interactions which may lead to adsorption, from very weak dispersion forces to different strengths and types of chemical bonding.

Physisorption is the result of a weak interaction between the absorbed molecule and the surface and hence, the heat of adsorption is rather low (Lüth, 1995). This weak interaction of this type, is the result of the electrical forces that appear between polar and neutral molecules and the surface. In the case of molecules that have a permanent dipole movement, the interaction between this dipole and the permanent as well as the induced surface dipole, results in an attractive force.

We must keep in mind that nowadays adsorption energy is not a valid criterion to distinguish between chemisorbed and physisorbed molecules. The weak desorption or dipolar forces responsible for physisorption implies that, no chemical bond is formed between the molecules and the surface. This means that the electric structure of the absorbed molecule remains virtually unmodified, upon adsorption and no significant mixing between orbits from the molecule and the substrate takes place.

For some molecules the interaction with the surface is much stronger and the adsorption energies are of the same order of magnitude, as the energy of a chemical bond. The interaction between these molecules and the surface is very different in nature to the Van der waal's forces, the adsorption process can be described as a true chemical reaction in which the surface is a reactant. The term used to describe this kind of adsorption is chemisorption or chemical adsorption. A new, clearly different “reaction product” is formed after chemisorption takes place, in this product the substrate takes a fundamental part, as any of the terms which build up the molecule. Chemisorption involves strong mixing of molecular and substrate orbits to form new bonding orbitals between them. This chemical bond involves the sharing of electronic density which must be provided by the reaction counterparts and thus the formation of the bond may produce some polarization of the absorbate.

The influence of the bond formed with the surface on the rest of the molecule may produce strong geometrical deformation and changes in vibrational spectra. This effect may even produce the dissociation of the absorbed molecule, a process called dissociative adsorption. The
Table 1. The fundamental differences between chemisorption and physisorption.

<table>
<thead>
<tr>
<th></th>
<th>Physisorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of interaction</td>
<td>Van der Waals</td>
<td>Covalent or ionic chemical bond, typically large, of the order of the chemical bond, several eV</td>
</tr>
<tr>
<td>Absorption energy</td>
<td>Less than 1eV</td>
<td></td>
</tr>
<tr>
<td>Molecular geometry</td>
<td>Mostly unmodified</td>
<td>Strongly modified molecule may dissociated</td>
</tr>
<tr>
<td>Vibrational spectrum</td>
<td>Very small shifts</td>
<td>Strong shifts in bonds which involve atoms bonded to the service</td>
</tr>
<tr>
<td>Orbital mixing</td>
<td>No mixing</td>
<td>Strong mixing of molecular orbital and metal states</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>No charge transfer</td>
<td>Charge transfer from molecule to service or vice versa</td>
</tr>
</tbody>
</table>

current criteria to distinguish chemisorptions from physisorption is not based on adsorption energy but on the formation or not of a true chemical bond between surface and adsorbate. The fundamental differences between chemisorptions and physisorption are shown in Table 1.

Adsorption in an electrochemical environment

From an electrochemical point of view, an extremely important species which deserves more attention in terms of adsorption, in what surface scientists would call a major contaminant present in all electrochemical experiments, the solvent. Water is in most cases the solvent selected to carry out electrochemistry but in spite of this, relatively little attention is given to the features of its interaction with the surface and with other adsorbates. Electrochemistry has an advantage over surface science to study processes in the surface, in that, the chemical potential of some adsorbed species can be easily controlled with a potentiostat. In surface science, equivalent control of the chemical potential of species in the gaseous phase requires precise control of the partial pressure. Clearly, the apparatus needed for either case differs drastically, potentiostatic experiments can be carried out far more easily. Furthermore, electrochemical potential of electrons depends linearly on potential. But chemical potential in the gaseous phase is proportional to the logarithm of the pressure.

In order to change significantly the chemical potential of a gaseous species, pressure must change several orders of magnitude while in electrochemical experiments just a fraction of a volt is enough. Another great advantage of electrochemistry over vacuum surface science is that, surface contamination from unwanted species can be easily reduced by protecting the surface with the solution. A major drawback is that, this protection introduces a new contaminant in enormous concentration, water. The electrochemical double layer owes its complex structure to a variety of adsorption phenomena of water and electrolyte species; furthermore, this structure changes drastically with the applied potential difference.

Adsorption and electro-catalysis

In chemical kinetics, it is common to compose a more or less complicated chemical reaction in a number of events, usually called elementary steps or simply reaction steps. Although, some simple electrochemical reactions exist where the main event may be described as a single electronic transfer, most of them involve some of the following processes:

1. Mass transport: This may affect reactants, intermediates of products and may occur via diffusion, convection or migration. The first concept refers to the random motion of particles, the second to the flow of the solvent and the third to the action of an electric field. Diffusion may occur in the neighborhood of the electrode, due to the depletion on accumulation of a species or on the surface.
2. Electronic transfer reaction: Nowadays it is accepted that the simultaneous transfer of two or more electrons is highly unlikely, so that each of a given reaction can be considered an elementary step. Every electrochemical reaction will involve at least one of these types of steps.
3. Chemical reactions: This may occur between species close to the surface or adsorbed on the surface.
4. Photochemical reactions: This is in the case where the system is being illuminated and some of the species are light sensitive.

In the case of semiconductors, light may also be used to promote electrons from a lower state (valence band) to higher energy levels (that is, conduction band).

These processes are usually sequential, that is, they are assumed to occur one after the other. Thus, it is also usual in electrochemistry to think of a given electrochemical reaction as a succession of steps, each
of which involves some of the processes mentioned above. For more details, the reader is advised to see Trasatti (2001) and Crow (1994).

Electrochemical reaction for which no adsorbed intermediate exists are extremely rare and the electrons transfer step or steps, almost always involve adsorbed species. This kind of electrochemical reaction for which, at least some intermediate is specifically adsorbed is called an inner sphere reaction. Outer reactions are those for which no specifically adsorbed intermediate exists, no near bonds are formed or broken and surfaces only provide an electron source. Unless the product clearly forms a new phase, as in the case of metallic deposition, inner sphere and outer sphere reactions cannot be distinguished by just looking at the global reaction. Even though the surface in this global reaction apparently is not involved, it is necessary for the development of the reaction.

In basic chemistry, these kind of species that are necessary for a reaction to take place but do not seem to participate in the global equation, are called catalysts. The kind of surface used to carry on the reaction is of uppermost importance. For example, the reverse of the reaction just described, the hydrogen evolution reaction occurs easily on platinum but is extremely slow on mercury. Since the metallic surface takes an active role in the formation of intermediates, the nature and particular state of the surface is crucial for the success of the reaction. The metallic surface is then an electrocatalyst, a catalyst for electron transfer reaction. If the rate determining step of the reaction involves an adsorbed species and this is probably the case, then the nature and structure of the metallic surface will determine the speed of the reaction.

Not only does the structure of the metallic surface change from metal to metal but also the structure of the solution side of the interface changes, mainly because the change in the potential of zero charge causes a change of the surface charge. This change of the potential of zero charge may be produced upon a specific surface by adsorption of a different metal with a different potential of zero charge. The challenge of theoretical electrocatalysis is to understand the way by which an electrocatalyst works, in order to improve it, to apply this knowledge to other similar systems. As in many cases, the steps in which the metal takes an active part in the electrochemical reaction, are adsorption processes.

Theoretical approaches to chemisorption

The interface is a highly anisotropic environment in which drastic changes of composition occur within a very narrow spatial extent. The abrupt differences in the molecular structure of the phases on either side of the interface, which makes them so interesting and rich in features. The electrochemical interface is particularly pathologic in this sense, when compared to the much simpler metal-gas interface. It puts together a handful of problems, that are huge scientific problems by themselves, interacting in a nonlinear way, namely an externally polarized metal surface, a highly complex liquid such as water, electron transfer, salvation dynamics and chemisorptions, to name only a few. This makes the theoretical description of the electrochemical interface a singular problem, so complex that the subject still remains in its very initial steps, in spite of the great effort dedicated to its study. In what follows, we will give a brief account of what we may call a “modern” theory of chemisorptions. This theory or group of models is nowadays more or less established, to study adsorption in the metal vacuum interphase but the task to extend the methods to the study of the electrochemical interphase, is still in its early stages.

There is no such thing as a single theory of chemisorption which can describe all possible processes and aspects. The description of such a complex phenomenon certainly cannot come from a single model or theory but from a group of them which are suited for the description of particular aspects of the problem. The methods used to describe chemisorptions from a theoretical point of view may be divided in three large groups:

1. Methods for the construction of potential energy surfaces and the study of the electronic structure such as the density functional theory;
2. Methods to describe equilibrium states and their properties such as the thermodynamic Monte Carlo or lattice gas approaches;
3. Methods to describe processes such as translation state theory, stochastic reaction theories, dynamics and molecular dynamics in their various forms.

Cost reduction of fuel cells

The high capital cost for fuel cells is by far the largest factor contributing to the limited market penetration of fuel cell technology. In order for fuel cells to compete realistically with contemporary power generation technology, they must become more competitive from the standpoint of both capital and installed cost (the cost per kilowatt required to purchase and install a power system). The high capital cost (on a $/kW basis) today has lead to a significant effort focused on cost reduction. Specific areas in which cost reductions are being investigated include:

1. Material reduction and exploration of lower-cost material alternatives.
2. Reducing the complexity of an integrated system.
3. Minimizing temperature constraints (which add complexity and cost to the system).
5. Increasing power density (footprint reduction).
6. Scaling up production to gain the benefit of economies of scale (volume) through increased market penetration.

**Conclusion**

This paper presents useful information on some fuel cell designs, characteristics and their applications. Looking at the enormous cost reductions necessary for fuel cell systems to compete with the traditional technologies and the risks involved in exploiting the economies of scale effects, one would expect the market diffusion of the mass-produced fuel cell in its stationary application as a co-generation unit but not as a mobile fuel cell in cars. Techno-economic analysis also suggest that substituting engine driven co-generation units and boilers would induce less change in value added among the different industrial branches than the mobile fuel cell would, simply because of the smaller market volumes involved.

There could be substantial structural changes in the industry and energy supplies within two decades, even if the production of the fuel cell systems remained in a country which traditionally drive trains, co-generation units or boilers are produced. Process-oriented industries, such as steel and light metal works, cold rolling mills and the chemical industry stand to gain from the traditional net value added; the losers are the car industry producing components of the internal combustion engine with a large value added and the electricity producing industry. The industry will both profit from the mobile fuel cell because of additional sales of the electric motor and the more complex control system and will forfeit generator capacities, for small co-generation units and conventional large power plants. As long as hydrogen is made from natural gas, possibly with an intermediate fuel such as methanol or syn-fuel, the mineral oil industries could become a substantial loser in the case of the mobile fuel cell. The electricity sector could also lose in the long-term, if stationary fuel cells not only replace small boilers but also start substituting mobile fuel cells when parking in the garage at home or at work.

The production of fuel cell systems holds great opportunities for first movers and employment would benefit, particularly in those countries that import high shares of energy needed. But as the first production lines of the stacks and reformers require a highly automated large scale production and the producers may be global companies, there is also the high risk that, the employment for producing fuel cells will be situated abroad. If the winning and losing industries are unevenly located in a country, there may also be regional imbalances in employment and economic prosperity which are not expected at present.

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